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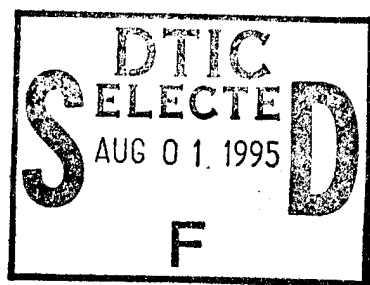
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The Role of the Metal in Determining Electrosorption Valency in the Case of Strong Molecular
Adsorption at the Electrode/Solution Interface

by

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13. ABSTRACT (Maximum 200 words) The electrosorption valency for the adsorption of parabonic acid has been determined on single crystal gold electrodes and mercury near the point of zero charge. A new technique to perform the measurement using cyclic voltammetry is described. The electrosorption valency was found to be a linear function both of the potential of zero charge and of the work function of the metal.					
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The Role of the Metal in Determining Electrosorption Valency in the Case of Strong Molecular Adsorption at the Electrode/Solution Interface

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Introduction

The use of single crystal electrodes has allowed the establishment of correlations between electronic and structural factors of the metal surface and electrochemical quantities [1,2]. In these studies, the electron work function and the potential of zero charge (pzc) have been used as important quantities to characterize the nature of the metal. Several relations between these two parameters have been suggested and they were used to obtain new information about the structure of the metal/electrolyte interface [3,4]. The shift of the pzc from one interface to another has been correlated to the shift of (i) the electron work function and (ii) a term concerning the solvent-metal interaction. One method of obtaining an insight into the contribution of the solvent term is the use of neutral compounds, which do not interact significantly with the metal, as probe molecules of the state of solvent at the interface [5-8]. In this sense, their free energy of adsorption was used to establish surface hydrophilicity scales [6].

The use of similar correlations for the case of molecules undergoing strong short-range interactions with the metal has been described very rarely [4,9]. However, these molecules are envisaged as good candidates to emphasize the parameters relevant to the metal, especially when one is interested in studying the effects due to crystallographic orientation.

Traditionally this type of study has been performed with the adsorbing species dissolved in the electrolyte solution. However, in the case of strong adsorbate-metal interaction some advantages can be gained by building the monolayer ex-situ, just as is done in a typical self-assembled monolayer experiment [10], and then to study the desorption process by continuous scanning cyclic voltammetry. In this way in the same

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single experiment it is possible to go from the high coverage situation to the limit of zero coverage. The reason for this is that when the species is desorbing and diffusing towards the bulk of the solution, its bulk concentration (initially zero) remains so low that the species is not undergoing the readsorption process to a significant extent. Otherwise, the change from high to low coverage would involve making several experiments with varying bulk concentration of the adsorbate.

In this preliminary note, results corresponding to the desorption process for parabanic acid (PA) adsorbed on different single crystal gold electrodes are presented. The dependence of the desorption peak potential extrapolated to zero coverage on the scan rate allows the estimation of the electrosorption valency. Attention is focussed on the correlation between this quantity, and both the potential of zero charge and the work function of the metal. Data for the adsorption of parabanic acid at the mercury/solution interface are also taken into account [11,12].

Experimental

Solutions of the supporting electrolyte (0.01M HClO_4) were prepared from redistilled 99.999% pure HClO_4 (Aldrich) and ultrapure water (17.8-18.0 $\text{M}\Omega\text{ cm}$). Parabanic acid was purchased from Sigma Chemical Co. and used without further purification.

Different faces ((111), (110) and (100)) of single crystal gold electrodes were used as the working electrode. The geometric area of these electrodes was $\approx 0.08\text{ cm}^2$. Procedures concerning their preparation, management and cleanliness have been described in previous papers [13]. The quality of each single crystal electrode was easily monitored by observing its cyclic voltammetric behavior in 0.01M HClO_4 before each experiment [13b]. A 0.05M KCl calomel electrode was used as reference electrode, and attached to the cell through a Luggin capillary containing the supporting electrolyte solution. In the present paper all potentials are reported with respect to this electrode, its potential being 120 mV positive of the saturated calomel electrode. The counter electrode was a gold wire of large surface area.

The formation of the monolayer was performed in the following way. The working electrode was immersed into a solution containing the surface-active molecule. Concentrations of parabanic acid greater than 10^{-5} M. were enough to obtain reproducible and concentration-independent results. After 5 minutes the electrode was removed, extensively washed with the electrolyte solution and transferred to the cell keeping on its surface a drop of liquid. Prior to measurements the solution was deaerated by passing argon for 8 min.

Cyclic voltammograms were obtained using a EG&G/PAR 273 potentiostat recording the output current and voltage using a BD 91 X-Y recorder (Kipp & Zonen). The sweep rate was varied in the interval from 0.01 to 2 Vs^{-1} .

Results and Discussion

Cyclic voltammograms for the parabanic acid system adsorbed on the (110) and (111) faces of a single crystal gold electrode are shown in Figure 1. These were obtained by continuously scanning the electrode potential in the double-layer region of the gold electrode starting at the most positive potential. The maximum surface excess, calculated from the theoretical molecular geometry [12], is 4.2×10^{-10} and 7.9×10^{-10} mol cm^{-2} for flat and perpendicular orientations, respectively. Whatever the orientation, the maximum charge involved in the current-potential curves ($q < 55 \mu\text{Ccm}^{-2}$ for (111) and (100) faces, and $q < 35 \mu\text{Ccm}^{-2}$ for (110)) is too small to correspond to a redox process, and it indicates that PA undergoes a desorption-adsorption process at the interface. Under these circumstances, the decrease of the current in successive scans arises from diffusion of some of the desorbed molecules towards the bulk, so that only a fraction of them are readsorbed in the backward sweep. The fact that the disappearance of the PA peak is coupled with the appearance of peaks corresponding to the capacity features of the gold/electrolyte interface in the absence of PA supports the desorption nature of this process. It should be noted that the first scan is somewhat different and more complex than the rest. This observation may be due to the existence of additional processes such as adsorbate reorientation and phase transitions [14-16]. These processes are known to operate under specific conditions at the interface, particularly at high coverage.

Therefore, in the remaining discussion we will focus on the limit of low coverage where single peaks are observed:

The desorption-adsorption process can be quantified using the electrosorption valency defined by Vetter and Schultze [17,18] according to the following thermodynamic relation:

$$\gamma = \frac{1}{F} \left(\frac{\partial \mu_{ad}}{\partial \Delta \phi} \right)_{\Gamma_{ad}} = - \frac{1}{F} \left(\frac{\partial q^M}{\partial \Gamma_{ad}} \right)_{\Delta \phi} \quad (1)$$

where Γ_{ad} and μ_{ad} are the surface excess and chemical potential of the species, respectively; q^M is the surface charge density on the metal and $\Delta \phi$ the rational potential. At the potential of zero charge ($\Delta \phi = 0$ and $\gamma = \gamma_N$) is interpreted in terms of molecular parameters:

$$\gamma_N = zg - \lambda(1 - g) + \kappa_{ad} - v\kappa_w \quad (2)$$

where z is the charge of the species, and λ is the partial charge transfer coefficient; κ_w and κ_{ad} are two terms arising from the contribution of the dipole moment of solvent and adsorbate, respectively; v is the number of solvent molecules replaced by one of adsorbate molecule, and g is a geometrical factor related to the distribution of potential at the interface. The dependence of the electrosorption valency on potential is given by the following equation:

$$\gamma = \gamma_N - \frac{1}{F} \int_0^{\Delta \phi} \left(\frac{\partial C_i}{\partial \Gamma_{ad}} \right)_{\Delta \phi} d\phi \quad (3)$$

where C_i is the inner layer capacity at a given surface concentration of the adsorbate. Thus the integral term is related to the change in the inner layer thickness when adsorbate molecules replace solvent molecules at the interface.

Traditionally the electrosorption valency has been determined from electrocapillary experiments by using eq. (1). Recently Szulborska and Baranski [19,20] developed a method to determine it from cyclic voltammetry. Assuming that (i) the adsorption process is reversible, (ii) the electrosorption valency does not depend on potential, and (iii) the interaction parameter between adsorbed molecules is negligible,

these authors [19] derived the following semi-empirical expression for the desorption peak potential extrapolated to zero coverage:

$$E_{d,\theta=0} = E^o + \frac{RT}{|\gamma_N|F} \left[0.46 + \ln \frac{1}{\rho_s} \left(\frac{DRT}{|\gamma_N|F} \right)^{1/2} \right] + \frac{RT}{|\gamma_N|F} \ln v^{-1/2} \quad (4)$$

where ρ_s is the diameter of the solvent molecule, D is the diffusion coefficient, v is the sweep rate and E^o is the potential at which the standard free energy of adsorption is equal to zero.

If the species is dissolved in solution application of eqn. (4) implies that the experiment be carried out with a low adsorbate concentration and that it be preconcentrated on the electrode by holding the electrode at a constant potential for a period of time. In this study the strong adsorption of PA at the gold electrode interfaces allows us to perform an alternative experiment, that is, to build the monolayer in a solution containing the adsorbate and then transfer the electrode to a cell containing only the electrolyte solution. In this way $E_{d,\theta=0}$ is estimated rapidly after a few potential cycles have been applied, since the coverage for successive scans under these conditions tends to zero. Figure (2) shows the dependence of the potential difference ($E_{d,\theta=0} - E_z$) on the logarithm of scan rate for the three different faces of gold single crystals. For the sake of comparison the potential scale is reported with respect to the potential of zero charge (E_z) for the pure electrolyte without adsorbate. The values of the electrosorption valency determined from the slopes of the straight lines on the basis of eqn. (4) are summarized in Table 1, where the minus sign was used since the desorption process is formally described as a reduction process. The linear relationship observed indicates that, at least over a certain potential range around the pzc ($|E - E_z| < 100\text{mV}$), the electrosorption valency is potential independent, and thus the integral term in eqn. (3) is negligible. However at more positive and negative potentials, a γ - E dependence may be expected whose determination would involve the analysis of a wider potential range. The present behavior contrasts with that observed for adsorption at the mercury/solution interface for which a lower and potential dependent electrosorption valency was found [12] ($\gamma_N = -0.012$, $(d\gamma/dE)_{E_z} = 0.57\text{V}^{-1}$). These results reveal the stronger character of the adsorption

process at the gold surface. As can be seen from Table 1, γ_N depends on the nature and crystallographic orientation of the metal surface, its absolute value increasing in the direction $(110) < (100) < (111)$. Taking the potential of zero charge as a macroscopic parameter to characterize the different interfaces, it was observed that the electrosorption valency depends linearly on it (Figure 3a).

In order to obtain an insight into the parameters affecting this dependence, γ_N is plotted (Figure 3b,c) against the different terms which contribute to the shift of the pzc from one interface to another [4]:

$$\Delta E_z = \Delta\Phi + \Delta X \quad (5)$$

where $\Delta\Phi$ stands for the change in the metallic work-function, and ΔX comes from the change in the solvent-metal interaction. For the present system a satisfactory linear relationship is obtained only in the case of $\Delta\Phi$. This behavior contrasts with that observed for physisorbed molecules on Hg and Au [6,8] for which the ΔX term has been addressed as the parameter ruling the adsorption process from one metal to another. This turns out to be a natural correlation, since in such systems adsorption is basically a solvent-substitution process. However, the above results indicate that for PA the principal factor determining the dependence of the electrosorption valency on the nature and crystallographic orientation of the metal is the metallic work function. From a molecular point of view and considering eqn. (2), such a dependence may be explained in two ways. If it is assumed the orientation of adsorbed PA is independent of crystallographic face, the variation in γ_N arises from a change in the partial charge transfer coefficient (λ). But if the molecule is oriented differently on each face, there will be an additional term arising from changes in the dipole moment contribution ($\kappa_{ad} - v\kappa_w$). The lack of a correlation with ΔX indicates that the contribution of the dipole moment terms is not playing an important role, and therefore it can be concluded that the γ_N against $\Delta\Phi$ dependence is a consequence of the increase in the partial charge transfer coefficient of PA with increase in the electronegativity of the metal, which in turn is correlated to the metallic work function.

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Table 1. Potential of zero charge and electrosorption valency of PA adsorbed on Hg and different single crystal gold electrodes.

Table 1

Electrode	$E_z(\text{calomel}, 0.05\text{M KCl}) / \text{V}$	γ_N
Hg	-0.549	-0.012 ^a
Au(110)	-0.170	-0.47
Au(100)	-0.070	-0.63
Au(111)	+0.110	-0.84

^a Taken from ref. 12.

Figure captions.

Figure 1. Cyclic voltammograms for (a) 110 and (b) 111 single crystal gold electrodes after dipping in 1.1mM PA/0.01M HClO₄ solution for 5 min. Arrows indicate evolution of the peaks under continuous scanning. For the sake of clarity the voltammograms corresponding to the (111) face were recorded only intermittantly after the seventh scan. Scan rate 100mV/s with initial negative-going direction.

Figure 2. Dependence of the rational desorption peak potential of PA, extrapolated to zero coverage, on the scan rate for the faces: (○) 110, (▽) 100 and (■) 111 of single crystal gold electrodes.

Figure 3. Correlation between the PA electrosorption valency and the shift of: (a) potential of zero charge, (b) work-function Φ and (c) the solvent-metal interaction term X , for different faces of single crystal gold electrodes taking as reference the values for the Hg/solution interface. Values for $\Delta\Phi$ and ΔX were taken from ref. 4. It should be noted that on the basis of the data presented in Figure 7 of this reference, the rows and columns in Table 1 seem to have been interchanged.

